Published in Annali di Chimica, v.93, pp.457-464 (2003).

INTER-ANNUAL VARIABILITY IN ATMOSPHERIC INPUT AND PARTITIONING OF HEAVY METALS IN THE LAGOON OF VENICE

Paolo ROSSINI[1], Stefano GUERZONI[2](°), Emanuela MOLINAROLI[3], Arianna ZANCANARO[4] and Giancarlo RAMPAZZO[3]

[1] Centro Studi Ambientali, via Al Torrente 22, 47900 Rimini
[2] CNR - Istituto di Biologia del Mare, Riva VII Martiri 1364/A, 30122 Venezia, and Istituto di Geologia Marina, via Gobetti 101, 40129 Bologna
[3] Università di Venezia, Dipartimento di Scienze Ambientali, Dorsoduro 2137, 30123 Venezia
[4] Comune di Venezia, Direzione Ambiente e Sicurezza del territorio, Via Palazzo 1, 30170 Mestre

Summary - Atmospheric bulk deposition of major and trace elements was measured at Venice from November 1995 to October 1997. Collection was carried out using polyethylene bulk passive samplers, samples being collected bi-weekly. In order to highlight the contribution of the atmosphere to water chemistry and particle budgets in the Lagoon of Venice, the geochemical composition (Si, Al, Ca, Mg, K, Na, Mn, Cr, Zn, Pb, Cd, Cu, As) of dissolved and insoluble bulk fractions was determined by AAS + ICP mass spectrometry. Great sample variability was found, with almost two orders of magnitude between maximum and minimum values for several metals. All fluxes in 1995/96 were 30% lower than in 1996/97, ranging from –3% (Ca) to –57% (Li), except for Zn, Cd and As. On the contrary, the solubility of all elements decreased during 1996/97. Partitioning between soluble and insoluble phases shows that Al, Cr, Fe and Si are mainly in the insoluble form, whereas for As, Ca, Cu, Mg, Na, Ni, K, Pb and Zn the dissolved fraction represents 50-90% of total input. The amount of particle load affects partitioning between dissolved and particulate, especially for Al and Pb. Seasonal variability was evident. The lowest pH values (~5.2) were recorded in winter, causing an increase of solubility for all metals except for As, which showed the highest solubility in summer.

Riassunto - In questa nota vengono presentati i dati di due anni di campionamento di metalli pesanti di origine atmosferica nelle deposizioni bulk a Venezia. La deposizione atmosferica degli elementi maggiori e degli elementi in traccia è stata raccolta ogni due settimane da novembre 1995 ad ottobre 1997 mediante campionatori passivi di tipo "bulk". La composizione geochimica (Si, Al, Ca, Mg, K, Na, Mn, Cr, Zn, Pb, Cd, Cu, As) delle frazioni bulk solubile ed insolubile è stata determinata tramite AAS + spettrometria di massa ICP. I risultati ottenuti indicano che quantità significative di Al, As, Cd, Co, Cr, Cu, Pb, Sb e Zn vengono rilasciate in laguna tramite la deposizione atmosferica. È stata rilevata una forte variabilità tra i campioni, con una differenza di almeno due ordini di grandezza tra i valori massimo e minimo per molti metalli. Ad eccezione di Zn, Cd e As, tutti i flussi sono risultati più bassi del 30% durante il primo anno di campionamento (1995-96) rispetto al secondo anno (1996-97), con variazioni a partire da –3% (Ca) fino a –57%

(°),Corresponding author. Fax (+39)- 041-520-4126. E-mail: guerzoni@ibm.ve.cnr.it

(Li). Al contrario, la solubilità di tutti gli elementi è diminuita durante il 1996-97. Lo studio della ripartizione tra le fasi solubile ed insolubile mostra che Al, Cr, Fe e Si si depositano principalmente in forma insolubile, mentre per As, Ca, Cu, Mg, Na, Ni, K, Pb e Zn la frazione solubile rappresenta il 50-90% dell'apporto totale. La quantità di particolato presente influenza la ripartizione tra fase solubile ed insolubile, soprattutto per Al e Pb. È evidente una certa variabilità stagionale. I valori più bassi di pH (~5,2) sono stati registrati in inverno, con un conseguente aumento della solubilità per tutti i metalli ad eccezione dell'As, che ha mostrato invece solubilità maggiori in estate.

INTRODUCTION

In the last few decades, actions for safeguarding the Lagoon of Venice have been mainly addressed to geomorphological and hydraulic intervention, almost completely neglecting the contribution of atmospheric deposition to the decrease in environmental quality.

Some atmospheric pollution surveys were conducted by Bertolaccini and Gucci over a 2-year period between 1973 and 1977[1,2]. They measured Fe, Mn, Pb, V and Cd contents in the atmospheric aerosol suspended particulate collected at three sampling sites in the Venice area: insular urban area (Venice city centre), industrial area (Marghera) and mainland urban area (Mestre). The highest concentrations of iron, manganese, vanadium and lead were found in the urban zone of the mainland, whereas cadmium exhibited different behaviour from that of the other metals, being higher in the insular urban zone.

Other works have been undertaken on a regional scale in order to assess the quality of rain,[3,4,5] and showed that the average rain composition approximated the nitrate/sulfate mixture with a volume-weighted average pH of 5.42 and a molar ratio NO_3^-/SO_4^{2-}, equal to 0.91.

In order to investigate the importance of atmospheric fall-out of pollutants to the lagoonal environment, since 1993 our group has been conducting studies on total atmospheric deposition using bulk samplers[6,7,8].

The aim of this paper is to present the data of 2-year bulk deposition sampling of heavy metals from the atmosphere, derived from bi-weekly collection in a station in the Lagoon of Venice.

EXPERIMENTAL

A total atmospheric deposition sampling station was set up at Venice (45°26’ N, 12°21’ E) from November 1995 to October 1997 (Fig. 1).

Atmospheric total deposition was collected by means of a bulk sampler,[9] composed of a polyethylene bottle with a polyethylene funnel (surface area = 0.065 m^2), placed inside a PVC container. The sampling equipment was mounted on a stainless steel support which, in order to avoid contamination, was painted with an inert varnish. Bulk deposition was sampled every two weeks. Sampling was carried out following protocols adopted by the WMO (World Meteorological Organization), for which the Institute of Marine Geology is a scientific consultant[10].

A total of 46 samples were collected over a two-year period: 24 samples from November 1995 to October 1996, and 22 samples from November 1996 to October 1997.

Physical-chemical parameters (pH and conductivity) were measured on samples immediately after collection. They were then filtered through 0.4 µm diameter Nuclepore© polycarbonate pre-weighed filters. Filtering was done with a Millipore© Sterifil unit, equipped with a pre-filter on the cover, to avoid contamination with ambient air. In order to obtain total particulate concentration,

the insoluble fraction was dried in a dry-box and re-weighed. Sampling blanks were collected by washing the polyethylene funnel of the sampler with 500 mL of Milli-Q^{TM} water (DDW), and laboratory blanks were also produced with DDW. The obtained solutions were then treated and analysed following the same procedures used for other samples.

Dissolved and particulate metal concentrations were determined by analysing the filtered and residual fractions. After dissolution in an acidic mixture, the insoluble fraction was digested in Teflon bottles in a microwave digestion unit. Soluble and insoluble fractions were analysed for major (Si, Al, Ca, Mg, K, Na) and trace elements (Mn, Cr, Zn, Pb, Cd, Cu, As) by AAS + ICP mass spectrometry.

All manipulations were conducted in a clean room equipped with a laminar flow bench.

RESULTS AND DISCUSSION

Variability of atmospheric deposition

In spite of the relatively long sampling period, great sample variability was found, with almost two orders of magnitude between maximum and minimum values for several metals. For example, total Pb fluxes ranged from 9 to 227 µg m^{-2} day^{-1}, Cd from 0.07 to 2.32 µg m^{-2} day^{-1}, and Na from 1 to 47 mg m^{-2} day^{-1}.

Figure 2 shows the mean atmospheric bulk fluxes measured at Venice. Annual fluxes of major elements ranged from 0.4 g m^{-2} y^{-1} for Al to 3 g m^{-2} y^{-1} for Na. Trace element fluxes fell between 0.3 mg m^{-2} y^{-1} for Cd, 18 mg m^{-2} y^{-1} for Pb, and 34 mg m^{-2} y^{-1} for Zn. All fluxes in 1995/96 were 30% lower than in 1996/97, ranging from –3% (Ca) to –57% (Li), except for Zn, Cd and As. In fact, as may be seen in Figure 2, all the elements are located over the 1:1 line, whereas Zn, Cd and As are positioned below, showing higher fluxes during the first year of sampling (Zn +3%, Cd +38% and As +10%) than in the second. Instead, the solubility of all elements decreased during 1996/97 (Figure 3). That is, total daily average fluxes of most metals were higher in the second year, whereas soluble fluxes were higher in the first (Table 1). During the study period, the observed solubility varied from ~5 % (Si, Al) to more than 80 % (Ca, Na, As, Cd).

The observed increases in pH (ranging from 5.53 in 1996 to 6.40 in 1997, see Figure 1) and the reduction in rainfall (from 850 mm in 1995/96 to 600 mm in 1996/97), clearly explain the decrease in soluble fraction fluxes in 1996/97. In general, the solubility of several elements increases with lowering pH[11,12]. In our case, for Pb, the pH=4 solubility ranged from 80 to 90 %, decreasing to 10-20 % at pH=6. The percentage of dissolved fractions of Al, Cd, Cr, Cu and Zn was also dependent on the pH value. For example, during the study period, Cr showed an inverse correlation with pH, with fluxes of dissolved Cr decreasing from ~35 %, at pH=4 to ~5 %, at pH>6.

In Table 2, data are combined in order to obtain mean seasonal fluxes and solubilities for the main elements. Values reported are the averages of seasonal fluxes observed during the two-year period of sampling. Seasonal variability is evident, especially in winter, when lower pH was recorded (mean pH = 5.07 in 1995/96 and 5.24 in 1996/97), and gave rise to the greatest solubility for all metals except As. This element showed its highest solubility in summer, when Zn and Cd showed their lowest. For Cd, the lowest deposition fluxes were recorded in summer.

The increase in solubility observed in autumn for almost all elements is probably due to a general decrease in particulate load. In fact, as reported by Guerzoni *et al*. (1999)[12] for dissolution in rainwater, with high particle concentrations the solubilities of Al, Fe, Pb and Cd decrease and, vice versa, increase with low loads.

Atmospheric loads

The degree to which a trace metal is enriched, relative to a specific source may be assessed approximately by using an enrichment factor (EF). For crustal sources, Al is normally used as the source indicator element and the Earth's crust as the source material[13]. The EF_{crust} value is then calculated according to an equation of the type: $EF_{crust} = (C_{xb}/C_{Alb})/(C_{xc}/C_{Alc})$, where C_{xb} and C_{Alb} are the concentrations of a trace metal x and Al, respectively, in a bulk sample, and C_{xc} and C_{Alc} are their concentrations in average crustal material[14].

Figure 4 shows that anthropogenic elements (mainly Pb, Cd, Cu and Zn) were anomalously enriched in both years, with the exception of Ni, which is assumed to have a significant crustal source. Enrichment in Ni with respect to continental crust concentration was observed during the first year of sampling. All EF values were higher in 1995-96 than in 1996-97.

In order to evaluate the importance of atmospheric fall-out of pollutants to the lagoonal environment, we calculated the supply rates of metals to the lagoon (surface area = 550 km^2) and compared them with riverine loads. Results are shown in Table 3. As may be seen, for Pb, Cd, Zn and Cu, the atmospheric loads are comparable to or higher than riverine ones.

CONCLUSIONS

- Partitioning of total atmospheric deposition between dissolved and insoluble phases shows that Al, Cr, Fe and Si are mostly in the insoluble form, whereas for the other metals studied (As, Ca, Cd, Cu, Mg, Na, Ni, K, Pb and Zn), the dissolved fraction represents 50-90 % of the total input.
- The solubility of the different metals depends mainly on pH, the amount, and the mineralogical characteristics of the particulate load.
- Significant amounts of Al, As, Cd, Co, Cr, Cu, Pb, Sb and Zn of anthropogenic origin are delivered into the Lagoon via atmospheric deposition; in particular, Pb, Cd, Cu, Ni and Zn were enriched from 17 (Ni) to more than 1000 times (Cd) with respect to average continental crust concentrations.
- The magnitude of atmospheric input indicates that eolian deposition is an important contribution which cannot be neglected in the study of biogeochemical cycles of anthropic elements introduced into the Lagoon of Venice. More studies are needed, with the deployment of several sampling stations around the Lagoon, in order to investigate site-to-site variability and to detect the sources of different metals. Comparisons with aerosol analyses will also help in defining the limits of concentrations in air and the role of the atmosphere in overall budgets.

Acknowledgements –This is IGM-CNR scientific contribution no. xxxx. Ms Gabriel Walton revised the English text.

REFERENCES

1) M. A. BERTOLACCINI and P. M. B. GUCCI, *Sci. Tot. Environ,* **43**, 243 (1985).
2) M. A. BERTOLACCINI and P. M. B. GUCCI, *Sci. Tot. Environ,*, **57**, 7 (1986).
3) F. ZILIO GRANDI and L. SZPYRKOWICZ, *Toxicol. Environ. Chem.*, **29**, 281 (1991).
4) F. ZILIO GRANDI and L. SZPYRKOWICZ, *Fres. J. Analyt. Chem.*, **341**, 625 (1991).
5) A ZANCANARO, Tesi di laurea, Università degli Studi di Venezia, Anno Accademico 1995-1996.

6) S.GUERZONI, E. MOLINAROLI, G. QUARANTOTTO and G. RAMPAZZO, *Plinius,* **14**, 177 (1995).
7) P. ROSSINI, S. GUERZONI, G. RAMPAZZO, G. QUARANTOTTO, E. GARIBBO AND E. MOLINAROLI, "Atmospheric deposition of trace metals in North Adriatic sea." In: E.M. Faranda, L. Guglielmo and G. Spezie (Editors), "*Mediterranean Ecosystem, Structures and Processes*", Springer Verlag Italia, 123 (2001).
8) P. ROSSINI, A. DE LAZZARI, S. GUERZONI, E. MOLINAROLI, G. RAMPAZZO AND A. ZANCANARO, *Annali di Chimica (Rome),* **91**, 491 (2001).
9) R. MOSELLO, A. MARCHETTO AND G.A. TARTARI, *Water Air Soil Pollut.,* **42,** 137 (1988).
10) WMO/UNEP-MAP, "MED-POL Manual on sampling and analysis of aerosols and precipitation for major ions and trace elements", MAP Technical report series, No. 123, Athens, 1998.
11) B.LIM, T.D. JICKELLS, J.L. COLIN AND R. LOSNO, *Global Biogeochem. Cycles*, **8**, 349 (1994).
12) S.GUERZONI, E. MOLINAROLI, P. ROSSINI, G. RAMPAZZO, G. QUARANTOTTO, G. DE FALCO AND S. CRISTINI, *Chemosphere*, **39**, 229 (1999).
13) S.R. TAYLOR, *Geochim. Cosmochim. Acta*, **28**, 1237 (1964).
14) S. GUERZONI, E. MOLINAROLI AND R. CHESTER, *Deep-Sea Res. II*, **44**, 631 (1997).
15) F. COLLAVINI, R. ZONTA, C. BETTIOL, O.E. FAGARAZZI AND L. ZAGGIA, "Metal and nutrient loads from the drainage basin to the venice lagoon." In: DRAIN - Project Workshop Proceedings, "*Determination Of The Pollutant Load Discharged Into The Venice Lagoon By The Drainage Basin*, Venice 14-15 June, 53 (2001).

FIG. 1 – Location of atmospheric deposition sampling site (white arrow).

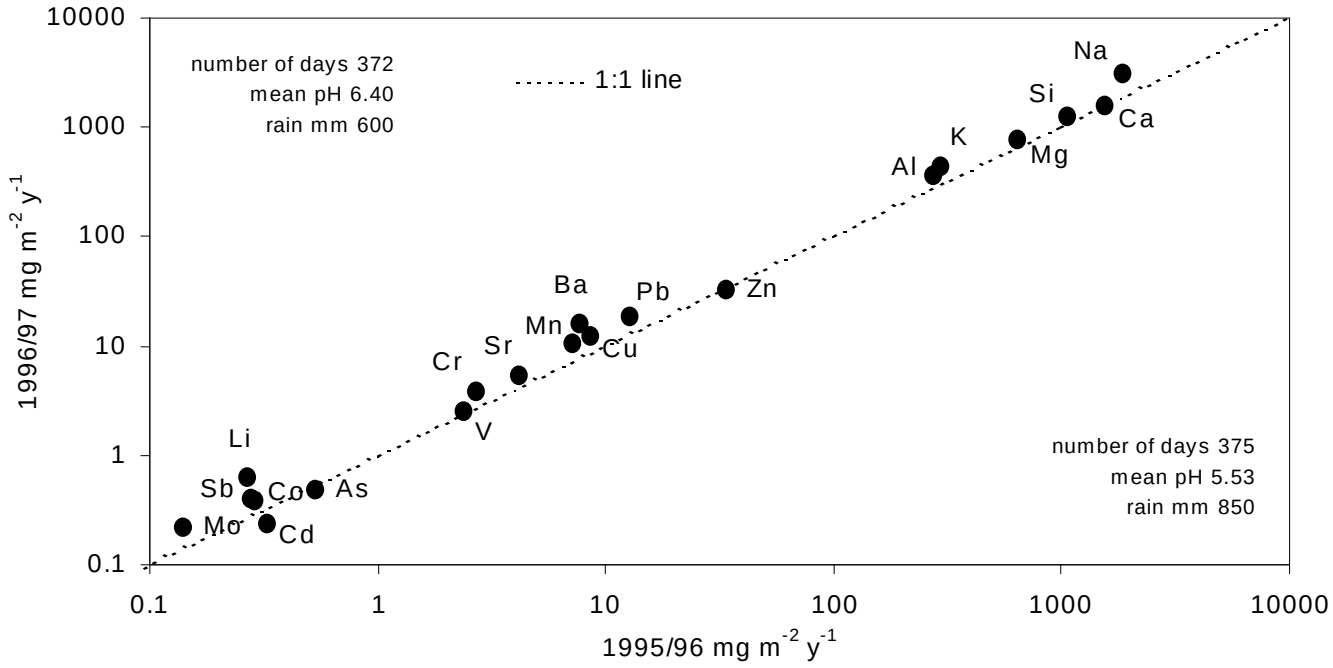

FIG. 2 – Total bulk fluxes observed during study period.

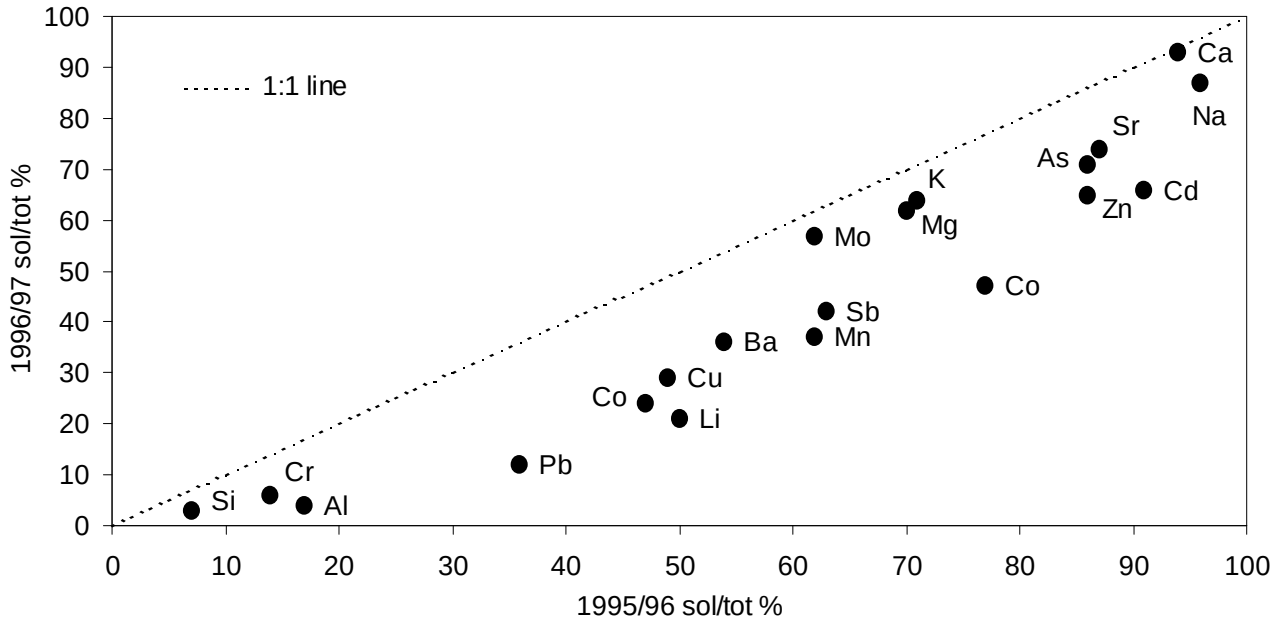

FIG. 3 – Solubility observed during study period.

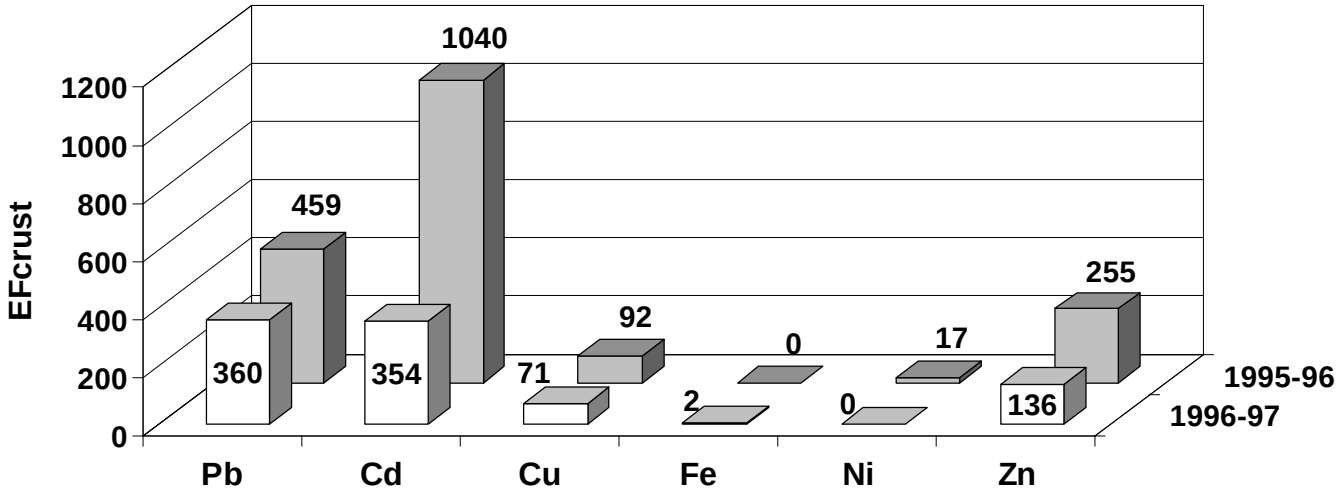

FIG. 4 – Crustal enrichment factors during study period.

TABLE 1 - Mean bulk daily fluxes at Venice. Tot = total (soluble+insoluble) fraction, sol = soluble fraction.

Element	Fraction	Fluxes µg m^{-2} d^{-1} 1995/96	1996/97	Element	Fraction	Fluxes µg m^{-2} d^{-1} 1995/96	1996/97
Na	tot	6023	7143	Zn	tot	100.71	92.26
	sol	5871	7052		sol	89.00	56.17
K	tot	1100	1274	Pb	tot	39.86	54.83
	sol	877	753		sol	20.14	6.32
Mg	tot	1858	2226	Cu	tot	27.13	35.67
	sol	1254	829		sol	16.41	10.42
Ca	tot	4486	4401	Cd	tot	0.92	0.65
	sol	4238	3965		sol	0.86	0.49
Si	tot	2800	3671	As	tot	1.61	1.39
	sol	159	111		sol	1.42	0.97
Al	tot	731	1049	Cr	tot	7.08	11.00
	sol	79	24		sol	0.66	0.54
Mn	tot	20.78	30.66				
	sol	13.52	9.69				

TABLE 2 - Mean bulk seasonal fluxes at Venice. Winter = November to January, spring = February to April, summer = May to July, autumn = August to October. Values represent average fluxes observed during both sampling years.

	units	winter	spring	summer	autumn
particulate	mg/l	20.00	20.67	18.78	9.10
pH		5.13	6.33	6.49	5.96
Na	µg m^{-2} d^{-1}	4291.7	3606.0	12427.7	5519.8
	solubility %	95.3	97.3	97.8	98.2
K	µg m^{-2} d^{-1}	952.7	773.2	1939.6	1003.0
	solubility %	76.8	60.2	60.7	64.8
Mg	µg m^{-2} d^{-1}	1477.4	1951.1	2975.3	1740.4
	solubility %	57.5	49.4	49.0	64.8
Ca	µg m^{-2} d^{-1}	2773.3	4557.1	6273.7	4325.1
	solubility %	95.5	88.7	95.8	93.6
Si	µg m^{-2} d^{-1}	2537.2	3831.7	4245.6	2336.6
	solubility %	4.6	3.3	5.1	7.8
Al	µg m^{-2} d^{-1}	815.5	887.2	1273.0	533.3
	solubility %	13.6	7.7	3.3	18.1
Zn	µg m^{-2} d^{-1}	83.6	90.7	131.5	79.6
	solubility %	82.8	70.0	68.3	80.0
Pb	µg m^{-2} d^{-1}	38.3	28.4	61.4	58.5
	solubility %	40.2	9.8	11.9	33.4

Cu	µg m^{-2} d^{-1}	31.9	27.6	27.5	37.7
	solubility %	56.6	29.6	28.0	46.6
Cd	µg m^{-2} d^{-1}	0.9	0.7	0.6	1.0
	solubility %	87.8	72.1	68.4	84.6
Cr	µg m^{-2} d^{-1}	9.8	9.7	10.2	5.9
	solubility %	15.7	3.7	4.4	16.5
Ni	µg m^{-2} d^{-1}	10.7	10.5	11.5	4.1
	solubility %	46.0	41.8	50.3	35.8
Fe	µg m^{-2} d^{-1}	1306.2	1033.1	1891.1	920.2
	solubility %	14.1	1.6	1.0	4.9
As	µg m^{-2} d^{-1}	2.0	1.3	1.4	1.2
	solubility %	82.8	63.6	83.0	81.3

TABLE 3. Supply rates of metals to Lagoon of Venice (tonnes y^{-1}). River data from Water Autority of Venice[15].

element	atmospheric deposition		rivers	
	total	soluble	total	soluble
As	0.3	0.2	4.6	4.0
Cd	0.14	0.13	0.06	0.03
Pb	8.6	2	3.0	0.3
Zn	19	14	18	6
Ni	1.8	1.1	3.9	2.4
Cu	6	2	7	3
Al	178	9	-	-
Co	0.2	0.1	-	-
Cr	1.7	0.1	3.5	1.0
Sb	0.2	0.1	-	-